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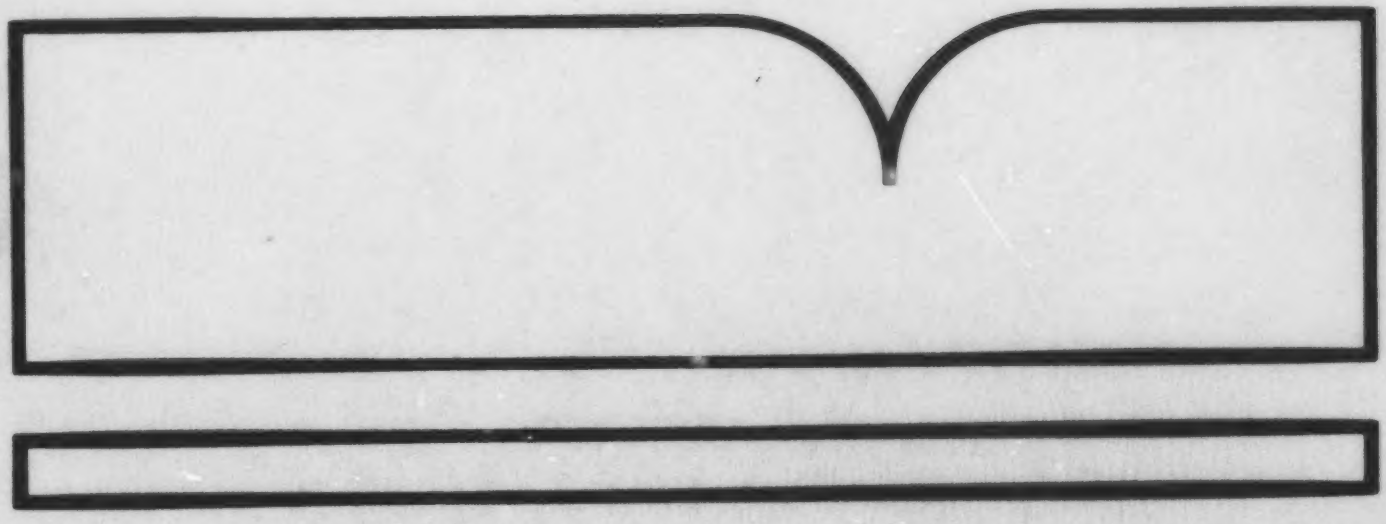

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16. ABSTRACT

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Geologic and Atmospheric Input Factors Affecting Watershed Chemistry in Upper Michigan

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ABSTRACT / The relationships between watershed variables and lakewater chemistry were examined for 53 lakes in the Upper Peninsula of Michigan to identify factors influencing lake sensitivity to atmospheric inputs. The lakes lie in three distinct geologic/geomorphic regions. Acid neutralization capacity (ANC), sulfate, and color were correlated with parameters related to atmospheric loading, watershed area and relief, hydrology, geology, and land use for the entire 53-lake set and for lower alkalinity subsets. Acid-neutralizing capacity was related to atmospheric acidic inputs and, in the southern portion of the Upper Peninsula, to the presence of mineralized groundwater inputs. In the north, ANC is correlated with hydrologic lake type and surficial deposits. Results show the highest density of acidified lakes in the northern region, which is underlain by noncalcareous sedimentary rocks. Color was related to lake size and the presence of organic soils in the watershed, whereas lake sulfate concentration was mainly influenced by atmospheric or groundwater inputs, surficial deposits, and soil type.

Introduction

Publications on aquatic resources at risk from acidic deposition in North America have usually referred to maps of igneous bedrock complexes, primarily the Canadian Shield, as mineralogic indicators of sensitivity (Kramer 1976, Galloway and Cowling 1978, Hendrey and others 1980). However, clastic sedimentary bedrock, particularly quartz sandstone and many shales, also may have no significant neutralizing capacity; thus, areas underlain by these bedrocks should be considered potentially at risk. These clastic sediments may occur in association with acid-neutralizing carbonate deposits, but the areal extent of acid-neutralizing potential through interactions with groundwater or glacial deposits needs to be evaluated. The eastern part of the Upper Peninsula (UP) of Michigan is subjected to significant acidic deposition (Glass and Loucks 1986), thus providing an area where the significance of poorly buffered sedimentary bedrock can be evaluated.

A program to investigate relationships among atmospheric deposition, watershed characteristics, and lake response in Michigan was undertaken by the University of Minnesota–Duluth (UMD) and the Environmental Research Laboratory–Duluth (ERL–D) during the period 1982–1985. Data were collected for 53 lakes in a five-county area of the Upper Peninsula with the goal of assessing the contribution of various watershed variables, including diverse bedrock types, in mediating atmospheric inputs and controlling resultant lakewater chemistry.

Research Framework and Hypothesis

To analyze the potential response of a watershed to changing atmospheric chemical inputs, a wide range of biogeochemical interactions must be considered. A series of processes and factors that influence lakewater chemistry have been identified in a number of recent studies (Seip 1980, Chen and others 1978, Schnoor and others 1986). Major processes affecting the geochemistry of water in a watershed include the wet and dry deposition of acidic and neutralizing substances, dilution and concentration during runoff and evaporation, terrestrial neutralization or mobilization due to weathering, anthropogenic influences, recharge and detention, and buffering and geochemical reactions occurring within the lake. These processes are represented in a conceptual model developed by Rapp and others (1985) that is based on nine classes of measurable watershed properties influencing lakewater chemistry:

	Watershed subsystems	Processes
1.	Atmospheric inputs	Deposition
2.	Topographic relief	Runoff
3.	Hydrology and renewal time	Recharge, detention

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4.	Lake morphometry	Evaporation, in-lake reactions
5.	Bedrock geology	Neutralization, mobilization
6.	Surficial deposits and landforms	Neutralization, mobilization
7.	Soils	Neutralization, mobilization
8.	Forest cover	Biological uptake, dry deposition
9.	Land use	Anthropogenic influence
10.	Lakewater chemistry	Result of watershed processes

The reaction rates for the processes listed above are tied to watershed size, the ratio of water surface area to terrestrial area, and the residence time of water within any component of the watershed. Although groundwater inputs and in-lake processes such as sediment–water interactions are important, they are not readily measured and were therefore not characterized as part of this study.

The general hypothesis of the study was that lakewater chemistry is a function of atmospheric inputs and biogeochemical reactions occurring as the water passes through the watershed. Our previous work identified alkalinity, sulfate, and color as three principal chemical measures reflecting lake sensitivity and the influence of various watershed factors and processes (Rapp and others 1985).

Alkalinity, a measure of available acid-neutralizing capacity (ANC), is recognized as an indicator of sensitivity (Henriksen 1980, Dillon and others 1978, Glass and others 1982). Fifteen of the Michigan lakes fall into the acid or extremely sensitive alkalinity range of Bangay and Riordan (1983).

The hypothesis being examined in this article is that the wet sulfate (SO_4^{2-}) deposition in the Upper Peninsula, about 18 kg $ha^{-1}yr^{-1}$ (Chan and others 1983, Glass and Loucks 1986), has led to SO_4^{2-} becoming the major anion in the aqueous component of the watershed where it replaces bicarbonate (Wright and Gjessing 1976, Dickson 1975). Excess sulfate has been closely tied to loss of bicarbonate alkalinity and the acidification of softwater lakes in regions underlain by igneous bedrock (Henriksen 1980).

Water color can be an indicator of dissolved humic acids (Dickson 1975, Heiskary and others 1982) and of the potential for metal and low pH buffering when organics are acidic or chelated with metals such as aluminum or iron (Dickson 1978, Johannessen 1980). In addition, low pH clearwater lakes also occur, often with high aluminum concentrations, reflecting the increased mobilization of this metal in association with low pH and strong acids (Dickson 1978). Thus an extension of the hypothesis being examined here is that humic acids also must be understood as a product of watershed processes with the potential to interact with SO_4^{2-}, H^+, and ANC. The question is whether the low pH in the clearwater systems may be the result of increased atmospheric acidic loadings and not organic acids.

In the carbonate bedrock areas of the Upper Peninsula, chloride concentration can be an important indicator of groundwater influx from bedrock; it also serves as an indicator of anthropogenic activities such as road de-icing or waste water treatment. Thus, high chloride will be considered as one indicator of anthropogenic activity throughout these analyses.

Methods

Watershed Characteristics

The significance of various hydrologic, geologic, biologic, and cultural parameters in watershed studies has been shown by the work of Eilers and others (1983), Lucas and Cowell (1984), and Galloway and Cowling (1978). Fifty-two watershed characteristics pertaining to size, topography, hydrology, bedrock geology, soils, vegetation, and anthropogenic influences have been defined, measured, and analyzed through cartographic and field methods as described by Rapp and others (1985).

Average evapotranspiration (ET) was estimated for the land area of each watershed using the long-term annual precipitation minus annual runoff values from Geraghty and others (1973) and Passero and others (1981). Individual values for watersheds were determined through interpolation between isopleth lines. The total annual atmospheric water yield was calculated for each watershed by summing the product of watershed land area times annual runoff and the product of lake surface area times the difference between precipitation and open water evaporation. Lakewater renewal time was estimated by dividing annual atmospheric water yield by lake volume. The evaporative concentration ratio (ECR) was calculated by dividing the product of total watershed area times precipitation by annual atmospheric water yield.

Because the actual water renewal time (WRT) for seepage lakes probably was somewhere between the values computed using annual water inputs from the total watershed area and from the lake surface area only, an alternative method of determining WRT was developed for lakes with no permanent surface inlets or outlets. This method was based on using concentrations of magnesium in lakewater as an indicator of groundwater inputs (Stauffer 1985) and was an attempt to differentiate more clearly between seepage

lakes supported by groundwater and those dominated by precipitation inputs. For seepage lakes with highest magnesium concentrations (i.e., $[Mg^{2+}]$ = 5.85 mg/L) water yield from the total watershed area was used for calculating WRT. For seepage lakes with lowest magnesium levels (i.e., $[Mg^{2+}]$ = 0.25 mg/L) water yield from the lake surface area only was used for calculating WRT. A linear interpolation was used for lakes with intermediate magnesium concentrations.

The ECR was used to predict, as a first approximation, the lakewater concentrations of ionic components derived from atmospheric inputs. The ECR was also computed from the ratio of chloride concentration measured in lakewaters to that in precipitation, assuming chloride to be "nonreactive" (Stauffer 1985). Wet atmospheric inputs for each watershed were determined using linear interpolation between isopleths derived from NADP monitoring data (NADP 1985, Glass and Loucks 1986). Dry deposition of sulfate was estimated to be an additional 19–24% depending on the magnitude of the wet deposition using the measurements of Chan and others (1984 and 1985) taken during 1981–82 in the study region. Acidic deposition was calculated using the method described by Glass and Loucks (1986), where both ammonium and nitrate ion concentrations are considered. The dry deposition of nitrate was estimated using the data of Chan and others (1984). The precipitation concentration value times the ECR for the watershed was used to predict lakewater concentrations of chloride and sulfate. The ratio of measured lakewater sulfate to that predicted from atmospheric inputs was calculated as the sulfate retention index (SRI). Procedures describing other key watershed variables (Table 1) are summarized by Rapp and others (1985).

Geologic Analysis

Bedrock, glacial deposit, and soil samples were collected in the study region during the summer of 1983. The rock samples were thin-sectioned, point-counted, and analyzed for Ca^{2+}/Mg^{2+} ratios and percentage of total sulfur (Technical Services Laboratory, Mississauga, Ont.). Pebble counts were made on the glacial till samples, and all surficial sediments were sieved for grain size analysis, point counts, Ca^{2+}/Mg^{2+} and sulfur analyses. Field descriptions, point counts, and percentage of total sulfur for sampled units are summarized in Table 2.

Water Quality Parameters

All water samples were analyzed in accordance with USEPA Methods for Chemical Analyses of Water and Waste (USEPA 1979). Sample collection, lab analyses, and quality assurance procedures are summarized by Rapp and others (1985).

The water quality data have been subjected to quality assurance procedures for single parameter measurements and interrelationships to determine outliers and systematic errors in measurement or manipulation using charge balance (APHA 1980), the calculated pH-ANC relationship (Stumm and Morgan 1981), and comparing measured versus calculated conductivity (Quint and Viallard 1978). The precision and accuracy (based on standard additions and USEPA and NBS standard samples) of these measurements are, on average, within 5% of expected values. The water chemical data are given as mean values averaged from all samples taken over the 2-yr period of study. The mean for pH values was determined by averaging hydrogen ion concentrations.

Statistical Analyses

The Michigan watershed and chemical data base was subjected initially to a battery of descriptive statistics (mean, standard deviation, etc.), N-score plots, and histograms using the MINITAB statistical package (Ryan and others 1976) to identify outliers and possible errors in coding or measurement. On the basis of the linearity of the N-score plots it was decided that several of the variables should be transformed before being used in regression analyses. The effect of the transformations was to "normalize" the distributions as required for correlation and regression analyses. The MINITAB runs, N-score plots, and transformation process were repeated on a 32-lake subset of lower ANC lakes (<500 ueq/L).

Once the appropriate transformations had been determined using N-score plots, correlation matrices were constructed to relate 160 watershed and water chemistry variables to each other. On the basis of the strength and significance of individual correlation coefficients in the matrices, lists of variables influencing ANC, color, and sulfate were compiled for the 53-lake set and two lower alkalinity subsets of 32 lakes (<500 ueq/L) and 23 lakes (<200 ueq/L). From these lists the final variables for multiple regression runs were chosen according to the requirements of the conceptual model that each watershed component and/or process be represented, if possible, by one variable which could be identified as varying independently from all other chosen variables. Following transformations and variable selection, multiple regression runs using BMDP9R (Dixon 1979) were made with each dependent variable (ANC, sulfate, color) against the chosen independent variables to generate a series of

Table 1. Summary of watershed characteristics for 53-lake and 32-lake sets in the Michigan Upper Peninsula.

Variable	N	Median	Mean	Minimum	Maximum	SD
Water chemistry						
ANC—ueq/L	53/32	245.4/57.5	1136.2/110.9	−38.0/−38.0	8719.6/480.5	1800/150
pH	53/32	6.8/6.0	6.6/6.0	4.4/4.4	8.2/7.3	1.0/0.9
Conductivity—uS/cm, 25° C	53/32	40.4/23.1	119.2/28.3	12.9/12.9	743.8/60.5	160/13
Color, unfiltered—Pt-Co units	53/32	20.1/16.3	29.3/26.2	2.5/2.5	150.0/150.0	30/29
SO_4^{2-}—mg/L	53/32	4.14/3.86	5.91/4.21	2.13/2.29	26.00/7.10	4.5/1.3
Area						
Lake surface—ha	53/32	36.9/25.3	52.3/38.6	3.5/3.5	310.2/198.4	54/41
Immediate watershed—ha	53/32	120.8/91.1	169.7/127.7	9.9/9.9	2021.9/327.7	270/88
Total watershed—ha	53/32	227.9/162.0	551.7/415.8	34.3/34.3	4491.1/4491.1	870/840
Total/surface area ratio	53/32	7.60/8.2	11.23/10.7	2.0/2.0	77.3/54.7	13/11
Atmospheric inputs						
Annual precipitation—m/yr	53/32	0.76/0.76	0.76/0.76	0.76/0.76	0.76/0.76	0.00/0.00
Annual evapotranspiration—m/yr	53/32	0.35/0.36	0.35/0.35	0.32/0.34	0.37/0.37	0.015/0.011
Annual wet sulfate dep.—ueq/L	53/32	45.0/44.5	45.9/44.9	43.0/43.0	51.6/47.8	2.4/1.3
Total acid dep.—ueq/L	53/32	35.7/35.4	36.8/35.8	34.0/34.0	42.8/38.8	2.5/1.3
Topographic relief						
Site elevation—m	53/32	244.8/248.5	235.4/241.0	178.3/190.2	278.3/278.3	32/31
Immediate watershed relief—m	53/32	16.5/15.8	20.6/21.9	0.0/0.0	97.8/97.8	20/24
Total watershed relief—m	53/32	21.3/16.9	29.6/27.0	0.9/0.9	97.8/97.8	24/26
Annual runoff—m/yr	53/32	0.41/0.41	0.41/0.41	0.39/0.39	0.44/0.43	0.015/0.011
Hydrology and renewal time						
Site order	53/32	1.0/1.0	1.4/1.3	1.0/1.0	4.0/3.0	0.7/0.6
Total streamflow magnitude—inlets	53/32	1.0/1.0	2.0/1.9	1.0/1.0	7.0/6.0	1.5/1.4
Total streamflow magnitude—outlets	53/32	1.0/1.0	1.6/1.4	1.0/1.0	4.0/4.0	1.0/0.9
Renewal time (Mg^{2+})—yrs	53/32	2.1/8.3	8.9/14.0	0.0/0.1	56.4/56.4	13/15
Lake morphometry						
Maximum depth—m	53/32	3.6/7.2	7.0/8.5	0.9/1.5	22.2/22.2	6.4/6.7
Mean depth—m	53/32	1.9/3.5	3.1/3.7	0.4/0.5	10.0/10.0	2.4/2.5
Volume—$m^3 \times 10^4$	53/32	72.4/68.4	145.9/134.9	3.9/3.9	868.6/497.9	160/130
Bedrock geology						
% scale 1 bedrock	53/32	100.0/0.0	50.9/34.4	0.0/0.0	100.0/100.0	51/48
% scale 3 bedrock	53/32	0.0/0.0	30.2/37.5	0.0/0.0	100.0/100.0	46/49
% scale 9 bedrock	53/32	0.0/0.0	18.9/28.1	0.0/0.0	100.0/100.0	40/46
Depth to bedrock[a]	53/32	4/6	4.19/5.16	0/0	9/9	3.1/2.6
Surficial deposits and landforms						
% loamy soil	53/32	0.0/0.0	9.5/0.0	0.0/0.0	86.9/0.0	24/0.0
% well-drained sandy soil	53/32	74.5/80.3	59.2/71.9	0.0/0.1	98.7/97.1	33/24
% nonacid organic soil	53/32	0.0/0.0	7.9/3.6	0.0/0.0	66.8/34.4	15/8.4
% acid organic soil	53/32	0.0/0.0	4.2/6.2	0.0/0.0	66.3/66.3	14/18
% clayey soil	53/32	0.0/0.0	1.1/0.0	0.0/0.0	23.7/0.0	4.0/0.0
% thin till over bedrock	53/32	0.0/0.0	11.3/0.0	0.0/0.0	100.0/0.0	32/0.0
% organic deposits	53/32	0.0/0.0	6.9/6.3	0.0/0.0	100.0/100.0	25/25
% lacustrine deposits	53/32	0.0/0.0	25.8/28.3	0.0/0.0	100.0/100.0	42/43
% outwash deposits	53/32	0.0/0.0	14.1/17.0	0.0/0.0	100.0/100.0	34/37
% calcareous moraine	53/32	0.0/0.0	5.7/3.1	0.0/0.0	100.0/100.0	23/18
% noncalcareous moraine	53/32	0.0/12.5	36.3/45.3	0.0/0.0	100.0/100.0	47/49
Forest cover						
% deciduous	53/32	56.0/48.7	52.1/48.3	0.0/0.0	100.0/100.0	32/35
% coniferous	53/32	44.0/51.4	47.9/51.7	0.0/0.0	100.0/100.0	32/35
Landcover and land use						
% forest	53/32	74.9/75.8	73.1/73.6	34.4/37.1	97.2/97.2	15/16
% water	53/32	14.1/15.1	17.2/17.8	2.8/2.8	45.4/45.4	9.9/11
% marsh	53/32	1.3/0.6	3.0/3.4	0.0/0.0	25.5/25.5	5.0/6.1
% urban residential	53/32	0.0/0.0	1.4/0.7	0.0/0.0	32.1/10.0	4.8/2.2
% pasture	53/32	0.0/0.0	4.2/3.9	0.0/0.0	49.6/49.6	9.7/11
% urban nonresidential	53/32	0.0/0.0	0.1/0.0	0.0/0.0	5.4/0.0	0.7/0.0
% transportation	53/32	0.0/0.0	0.1/0.0	0.0/0.0	2.4/0.0	0.5/0.0
% extractive & cultivated	53/32	0.0/0.0	1.0/0.6	0.0/0.0	19.8/19.8	3.4/3.5
% cultural development	53/32	0.8/0.0	6.7/5.2	0.0/0.0	49.6/49.6	11/11

Table 1. *Continued.*

Variable	N	Median	Mean	Minimum	Maximum	SD
Dwelling count	53/32	2.0/1.5	7.1/4.4	0.0/0.0	80.0/35.0	15/8.0
Dwelling ratio	53/32	0.05/0.07	0.15/0.13	0.00/0.00	1.16/0.69	0.24/0.19
Light road length—km	53/32	0.0/0.0	0.5/0.4	0.0/0.0	6.0/2.3	1.0/0.6
Unimproved road length—km	53/32	0.3/0.3	1.0/0.7	0.0/0.0	17.5/2.5	2.4/0.8
Light road distance—km	21/13[b]	0.0/0.0	0.03/0.05	0.0/0.0	0.2/0.2	0.07/0.08
Unimproved road distance—km	35/22[c]	0.0/0.0	0.01/0.01	0.0/0.0	0.2/0.2	0.04/0.04
Total road length—km	53/32[d]	0.7/0.8	1.5/1.1	0.0/0.0	23.5/2.9	3.3/1.0

[a] 0 = 0–4 m; 1 = 5–9 m; 2 = 10–14 m; 3 = 15–19 m; 4 = 20–24 m; 5 = 25–29 m; 6 = 30–34 m; 7 = 35–39 m; 8 = 40–44 m; 9 = 45+

[b] Evaporative concentration ratio computed using chloride in lake and precipitation water. The 32 sites without other sources of chloride inputs were included; SRI computed for same 32 sites.

[c] Only 21 and 35 watersheds respectively included any light or unimproved roads.

[d] 38 watersheds included some type of road.

Table 2. Composition of Michigan rock and surficial samples.

Sample	Description	% S	Composition (from point counts)
Miner's castle sandstone (Cambrian)	Thinly bedded, reddish-brown, coarse-grained, quartz-rich sandstone, noncalcareous		86% Quartz; poorly sorted, highly fractured 11% Biotite–chlorite cement 3% Chert, perthite, opaques, felsics, rock fragments
Chapel rock sandstone (Cambrian)	Pale buff, medium-grained sandstone, noncalcareous		86% Quartz; well-sorted, highly fractured, well-rounded 11% Biotite–chlorite cement 1% Opaques, felsics, hematite
Black River/ Trenton group (Ordovician)	Dark gray calcareous, slightly recrystallized, Fe-rich weathering rind	0.21	100% calcite
Manitoulin dolomite (Ordovician)	Pale buff dolomite, unevenly bedded, beds approx. 15.24 cm (6") thick	<0.01	100% calcite
Hendricks dolomite (Silurian)	Buff to pale gray fossiliferous dolomite, coarse to thinly laminated, finer towards top	0.01	100% calcite
Fibron limestone (Silurian)	Pale buff, fine-grained limestone, with coarse recrystallized calcite crystals	<0.01	100% calcite
Schoolcraft dolomite (Silurian)	Pale buff to bluish massive dolomite	<0.01	100% calcite
Cordell dolomite (Silurian)	1) Buff to brown dolomite with abundant chert; fossils	0.02	100% calcite
	2) Buff dolomite with chert nodules and abundant fossils	<0.01	83% calcite 9% chalcedony 7% quartz
Engadine dolomite (Silurian)	1) Pale gray to buff, very hard dolomite, slightly recrystallized	<0.01	100% calcite
	2) Medium gray, fine-grained massive dolomite	<0.01	100% calcite
Newberry moraine	Fine-grained, water-lain sand to clast supported till	0.03	Pebbles include sandstone, limestone, mudstone, granite, basalt, amphibolite, schist
Munising moraine	Sandy till, sand-supported; matrix noncalcareous	0.07	Pebbles include sandstone, limestone, amphibolite, granite, schist

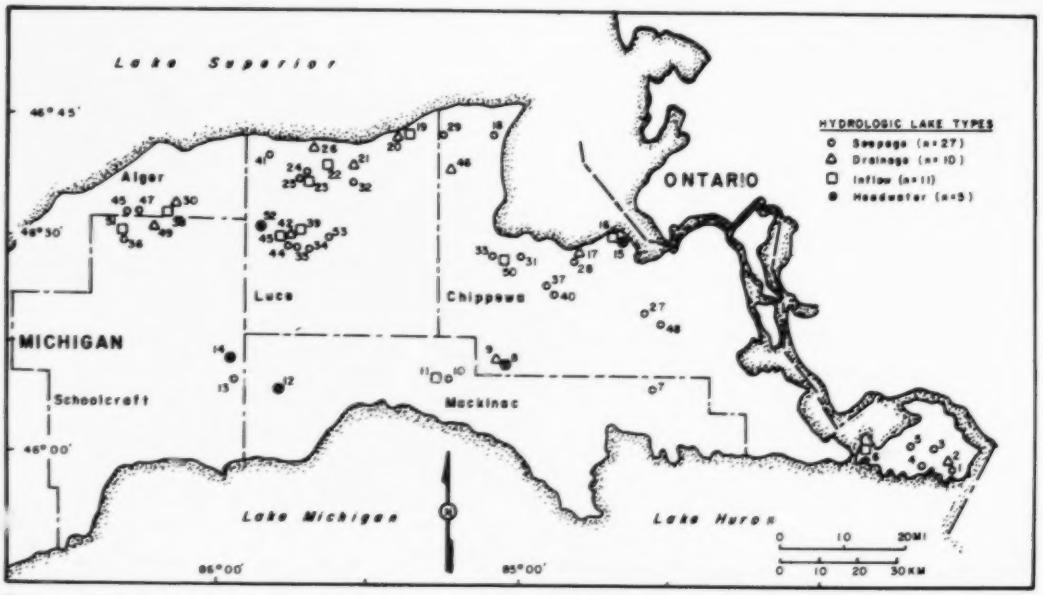

Figure 1. Site location and hydrologic lake type for 53 study lakes in the eastern Upper Peninsula.

best subsets to delineate potential relationships among the variables.

Study Area and Watershed Characteristics

The study region stretches 200 km east–west and 100 km north–south across Chippewa, Mackinac, Luce, Alger, and Schoolcraft counties in the eastern Upper Peninsula of Michigan (Fig. 1). The 53 lakes sampled during 1982 and 1983 are representative of the smaller lakes in the region. Many of the study lakes are located in the Hiawatha National Forest or in state forests and are relatively free of direct anthropogenic influences. The area is sparsely populated, with approximately 65,000 people (or 10 persons per 2.6 km^2 [1 mi^2]) living in the five-county area (UPRCDC 1973).

Because of the influence of the Great Lakes, the Upper Peninsula experiences a marine-like climate despite its mid-continent location. In the eastern Upper Peninsula, particularly near the shore of Lake Superior, temperatures are moderated, the growing season is extended (to 140–160 days), and snowfall is increased (to more than 250 cm annually), compared with typical continental locations at this latitude. Annual precipitation is about 76 cm; approximately half falls during the growing season (Strommen 1967).

Approximately 4% of the five-county region is covered by inland open water, with 93% of all inland lakes less than 250 ha in size (UPRCDC 1973). Although the majority of lakes in the region have small surface areas, they are diverse in morphometry, watershed characteristics, and water chemistry. Our set of study watersheds was nonrandomly selected to reflect this diversity and to encompass a range in location, size, lake type, depth, geology, and water chemistry (Table 1).

The topography of the area, a result of Late Wisconsin glaciation, is generally low relief with most of the watersheds less than 305 m above sea level (less than 122 m above the present Great Lakes) (Vanlier 1959, Vanlier and Deutsch 1958a and 1958b). The glacial deposits in this area reach thicknesses of up to 100 m in the north, but are thin to absent in the southern part of the Upper Peninsula. About 20% of the lakes studied are located in areas where glacial drift is less than 5 m thick; these lakes are situated in carbonate bedrock with high acid-neutralizing capacity. Much of the region is covered by lake plain and outwash deposits although there are three moraine systems in the northern part of the peninsula (Fig. 2).

The moraines, which were water-laid, are better sorted and stratified than those deposited on land and have been modified by wave action and subsequent deposition. The Newberry, Munising, and Crisp Point moraines run east–west across Alger, Luce, and Chippewa counties and are comprised primarily of quartz, feldspar, and granitic rock fragments derived from bedrock to the north. Samples from the Newberry and Munising moraines analyzed as part of this study had low sulfur and carbonate content (Table 2). The Mun-

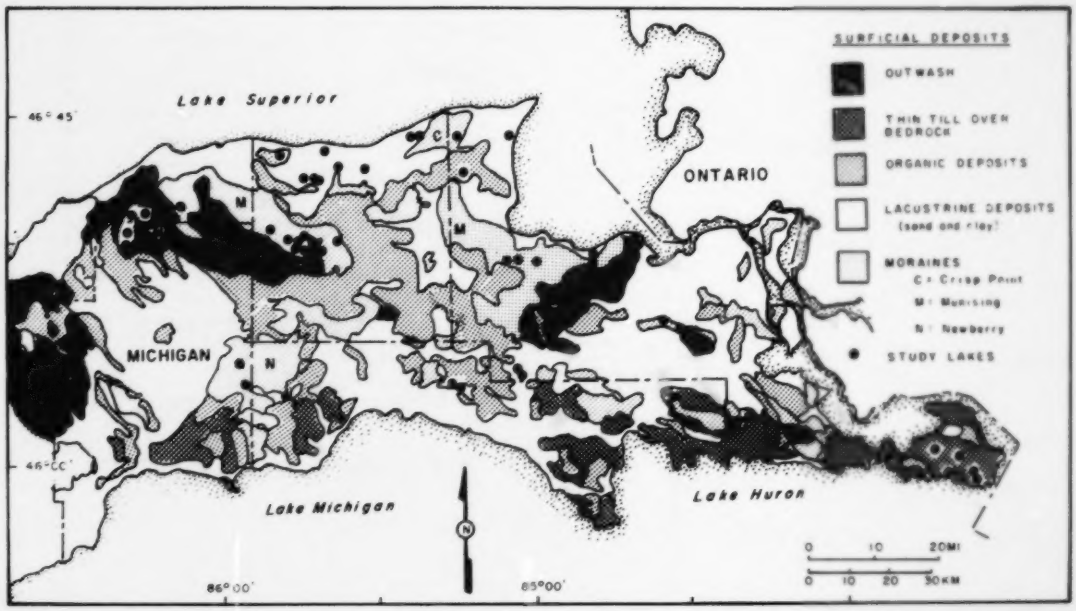

Figure 2. Quaternary deposits and location of 53 study lakes in the eastern Upper Peninsula (after Farrand and Bell 1982).

ising and Crisp Point moraines had the pure quartz Jacobsville and Munising arenites as source areas (Vanlier 1959, Vanlier and Deutsch 1958a and 1958b) and are composed of deposits that contain almost no neutralizing capacity. The Newberry moraine, older and farther south, is characterized by samples containing 1.5–15% calcareous material, derived from the Black River–Trenton Formation, which locally provides limited neutralizing ability.

Soil development and, consequently, vegetation and land use are closely related to the nature of the glacial deposits: poorly drained, organic, often acid soils develop in the lacustrine clays; well-drained, sandy soils form in areas of outwash; and loamier soils are found in morainic regions. Ninety % of the Upper Peninsula is forested: two-thirds northern hardwoods and one-third swamp and upland conifers. Much of the original forest was harvested and most of the present forest is second growth (UPRCDC 1973).

The region is underlain by Paleozoic sedimentary bedrock laid down in the Michigan basin. The strata dip to the south and are exposed in nearly concentric bands across the Upper Peninsula with older Cambrian rocks to the north and younger Silurian rocks to the south (Figs. 3 and 4). All the formations are carbonates with the exception of the Jacobsville and Munising sandstones (Cambrian). Our analyses of samples from the Miner's Castle and Chapel Rock members of these formations show them to be nearly pure quartz sandstones with little neutralizing capacity (Table 2). These rocks are the source for much of the material in the Crisp Point, Munising, and Newberry moraines, and, except near Tahquamenon Falls, are deeply buried.

Samples taken from the Ordovician and Silurian bedrock farther south were highly calcareous with very low levels of sulfur (Table 2). The Black River and Trenton Formations (Ordovician) are generally well buried beneath glacial drift and are exposed only in river valleys. A sample from the Black River formation had the highest percentage of sulfur (0.21%) of any rocks sampled. Although no samples were taken of the Richmond group shales, they are also calcareous (Ehlers and Kesling 1957), and would be expected to supply some neutralizing capability. The Middle Silurian rocks of the Niagara series are predominantly limestone and often form cuestas or escarpments with steep north-facing and more gentle southern dipslopes that run east–west across Mackinac and Chippewa counties.

Throughout the eastern Upper Peninsula, groundwater is available from aquifers in unconsolidated and consolidated sediments. In the northern half of the Upper Peninsula, Cambrian sandstones and Ordovician limestones and dolomites yield good groundwater supplies, although they are rarely tapped because of the accessibility of groundwater from the overlying glacial deposits. The Silurian carbonate strata to the

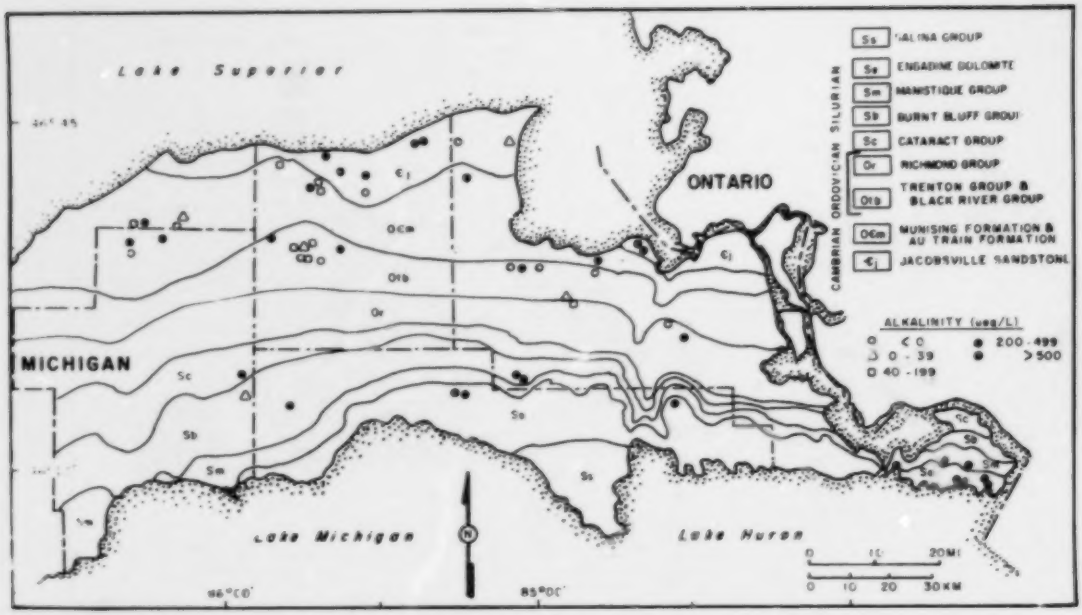

Figure 3. Bedrock geology and alkalinity of 53 study lakes in the eastern Upper Peninsula.

Geologic Time Unit: ERA	PERIOD	EPOCH	TIME - ROCK SERIES	THICKNESS MAX. (FEET)	LITHOLOGY	ROCK - STRATIGRAPHIC UNIT: MEMBER	FORMATION	GROUP
PALEOZOIC ERA	SILURIAN	LATE	CAYUGAN	300			MACKINAC BRECCIA	SALINA
				600			SAINT IGNACE DOLOMITE; POINT AUX CHENES FORMATION	
		MIDDLE	NIAGARAN	250			ENGADINE DOLOMITE	MANISTIQUE
				150			CORDELL DOLOMITE	
				60			SCHOOLCRAFT DOLOMITE	
				120		FIBRON LIMESTONE	HENDRICKS DOLOMITE	BURNT BLUFF
				155			BYRON DOLOMITE	
				35			LIME ISLAND DOLOMITE	
		EAR.	ALEXANDRIAN	250			CABOT HEAD SHALE	CATARACT
				50			MANITOULIN DOLOMITE	
	ORDOVICIAN	LATE	CINCINNATIAN	300			BIG HILL FORMATION	RICHMOND
						OGONTZ CHERTY LS.	STONINGTON FORMATION	
						BAY DE NOC SHALY LS.		
				260		COLLINGWOOD	BILL'S CREEK FORMATION	
		MID-DLE	MOHAWKIAN	300			GROOS QUARRY FORMATION	TRENTON
							CHANDLER FALLS FORM.	
							BOIS BLANC FORMATION	BLACK RIVER
		EAR.	ST. CROIXAN	300			AU TRAIN FORMATION	LAKE SUPERIOR
	CAMBRIAN	LATE		250		MINER'S CASTLE SS.	MUNISING FORMATION	
						CHAPEL ROCK SS.		
		EARLY & MIDDLE		1500			JACOBSVILLE SANDSTONE	
PRE - CAMBRIAN								

Figure 4. Stratigraphic section in the eastern Upper Peninsula (Goldman 1976).

south also provide large quantities of groundwater, but this water often is mineralized with high calcium-magnesium or calcium-sulfate contents. In the Salina, Ignace, and Bois Blanc formations underlying the southernmost part of the area, evaporative deposits are found, but were not sampled as part of this study. These contain gypsum and frequently yield groundwater with high calcium, chloride, and sulfate content

(Vanlier and Deutsch 1958b). Due to complex patterns of groundwater migration through adjacent bedrock aquifers and percolation through unconsolidated surficial deposits, local surface waters also may have very high mineral content, particularly sulfate and chloride (Passero and others 1981).

During the late 1800s and early 1900s copper smelting was common in the Keewenaw region of the Upper Peninsula and from 1865 to 1868 smelting occurred near Fayette in Delta County, west of the study area. Currently, major smelters are operating in Sudbury, Ontario, about 350 km east and in Wawa, Ontario about 200 km north of the area. Regional weather patterns are such that there is deposition from long-range atmospheric transport of sulfate and other components into the area from these current remote smelting operations (Chan and others 1985).

Results and Discussion

Watershed Parameters and Variability

The overall patterns among the lake and watershed descriptors are summarized in Table 1. The lakes range in surface area from 3.5 ha to 310.2 ha and in maximum depth from 0.9 m to 22.2 m. They are predominantly seepage lakes ($n = 27$) with no permanent surface inlets or outlets, some drainage lakes ($n = 10$) with both inlets and outlets; inflow lakes ($n = 11$) with inlets, but no outlets; and headwater lakes ($n = 5$) with no inlets and perennial outlets (see Eilers and others 1983). Morphometry is generally the result of glacial action, and regional drainage is to lakes Superior, Huron, or Michigan either through major river systems such as the Pine or Tahquamenon or through small streams flowing directly into the Great Lakes. Watershed areas vary from 34.3 ha to 4500 ha and estimated lakewater renewal times vary from 0.0 yr to 56.4 yr. Calculated hydrologic evaporative concentration ratios range from 1.9 to 2.8, and sulfate retention indices (SRI) range from 0.4 to 4.3.

The study lakes are characterized by great variability in most of the water chemistry parameters. ANC ranges from −38 to 8700 ueq/L, pH from 4.4 to 8.2, color from 2.5 to 150 PCU, and sulfate concentrations from 2.1 to 26.0 mg/L. Lakewater chemistry is strongly tied to a broad pattern of geographic location, proximity to carbonate bedrock, and associated groundwater interaction. (Complete site-specific water quality data and watershed characteristics are available from G. E. Glass.)

Evaporative Concentration Ratio

To more clearly identify sensitive lakes potentially dominated by precipitation inputs and to compare them with lakes having a high acid-neutralizing capacity, the magnitude of ionic concentration through evaporation had to be considered. Accordingly, a hydrologic evaporative concentration ratio (ECR) was calculated for each lake on the basis of atmospheric inputs and estimated lake evapotranspiration and was compared with an ECR calculated from Cl^- concentrations in precipitation and lakewater. As a first approximation, Cl^- was assumed to be a conservative ion with no sources or sinks in the watershed. The ECR values derived for each lake from both calculations are given in Table 3. The very high values of ECR based on chloride are obviously influenced by local sources of Cl^-, such as highly mineralized groundwater from the Upper Silurian evaporite deposits and/or from road de-icing. Consideration of lakes remote from these mineralized groundwaters or from anthropogenic influence indicates that Cl^- values of less than 10.0 ueq/L are probably free of groundwater or road-salting influences. All lakes with Cl^- less than 10.0 ueq/L were averaged to give a single regional ECR (chloride based) value of 2.2, the same average value derived from the hydrologic information.

The role of evapotranspiration on other substances entering with precipitation was evaluated using the ECR. The expected concentrations of sulfate from precipitation concentration were calculated using the ECR derived for each watershed and show sulfate retention in the watersheds to average 75%, excluding lakes with apparent groundwater inputs. Study lakes with SRI values substantially greater than 1.5 indicated sulfate sources other than the atmosphere, such as groundwater inputs and weathering processes in the watershed. Low SRI values (Table 3) can be caused by anaerobic sulfate reduction known to occur in bottom sediments and pore waters (Stumm and Morgan 1981, Schnoor and Stumm 1984, Schindler and others 1980).

Contrasts Between Three Geologic/Geomorphic Regions

The geomorphic landscape in the Upper Peninsula can be correlated with geology and lakewater chemistry. In the southern UP, where surficial geology is dominated by carbonate bedrock and thin-to-absent calcareous till, lakes have high acid-neutralizing capacity and are dominated by mineralized groundwater inputs. To the north, two other distinct landform types occur: glacial lacustrine deposits near the Lake Superior shoreline and noncalcareous moraine on the higher terrain between the two Great Lakes. The three regions differ distinctly in terms of the mineralogy of surficial and bedrock deposits as well as depth to bedrock, soil type, site elevation, and hydrologic drainage

Table 3. Three categories of Michigan study lakes based on geologic/geomorphic region.

ID #	Name	County	Latitude	Longitude	Hydrologic type	Lake elev	Depth bedrk	Org soils	Lacus deposits	NonCal moraine	ANC	pH	Color	Evap.-conc. ratio	Cl^- based ECR	Sulfate retention index
Shallow calcareous till																
1	Bass	Chippewa	455544	833332	Seepage	183	1	0.0	0.0	0.0	3500	8.0	23.0	2.6	7.3	1.9
2	Dickenson	Chippewa	455710	833417	Drainage	194	1	0.0	0.0	0.0	7100	7.5	25.0	2.2	10.6	2.9
3	Dry	Chippewa	455900	833650	Seepage	212	1	0.0	0.0	0.0	2500	8.2	15.0	2.4	5.3	1.2
4	Toivola	Chippewa	455717	833902	Seepage	182	1	0.0	0.0	0.0	4200	7.9	28.0	2.2	9.9	1.7
5	Marl	Chippewa	455958	834134	Seepage	197	1	0.0	0.0	0.0	8700	7.5	25.0	2.2	19.3	4.2
6	Parish	Chippewa	455840	835059	Inflow	178	1	0.0	0.0	0.0	4400	7.8	19.0	2.2	44.6	3.2
7	Hill	Mackinac	460745	843200	Seepage	260	5	0.0	0.0	0.0	3600	7.8	15.0	2.1	10.0	1.8
8	Wegwaas	Chippewa	461045	850030	Spring	259	1	22.8	100.0	0.0	2100	7.8	21.0	1.9	24.6	0.7
9	Frenchman	Chippewa	461100	850100	Drainage	251	1	18.5	100.0	0.0	3200	7.7	50.0	1.9	16.2	0.4
10	Strouble	Mackinac	460850	851148	Seepage	260	1	29.3	35.0	0.0	1100	7.1	40.0	2.2	14.4	1.3
11	Crossville	Mackinac	460914	851326	Inflow	260	1	54.9	0.0	0.0	2300	6.9	150.0	1.9	23.9	0.7
12	Mitten	Mackinac	460710	854515	Spring	218	15	52.5	100.0	0.0	3500	7.1	50.0	2.4	7.2	1.7
13	Tee	Schoolcraft	460858	855243	Seepage	225	20	0.0	0.0	0.0	37	5.8	25.0	2.6	3.2	0.6
14	Stewart	Schoolcraft	461137	855355	Spring	209	20	66.8	0.0	0.0	2600	7.1	50.0	2.4	39.0	1.7
Lacustrine deposits																
15	Spectacle	Chippewa	462740	843800	Spring	196	35	34.4	80.0	20.0	470	6.9	38.0	2.4	2.8	0.8
16	Monocle	Chippewa	462830	843845	Inflow	195	35	18.4	75.0	25.0	240	7.0	13.0	2.2	2.8	0.9
17	Pendills	Chippewa	462630	844630	Drainage	197	60	13.7	25.0	75.0	840	6.7	58.0	2.1	3.9	1.0
18	Andrus	Chippewa	464200	850225	Seepage	190	15	0.0	100.0	0.0	7	5.5	18.0	2.3	3.2	1.2
19	Bodi	Luce	464203	851935	Inflow	195	10	5.8	75.0	25.0	330	7.2	30.0	2.3	3.0	1.0
20	Culhane	Luce	464137	852112	Drainage	191	10	16.1	75.0	25.0	480	7.3	75.0	2.2	2.5	0.7
21	Chris Brown	Luce	463734	853027	Drainage	215	30	0.0	100.0	0.0	200	6.9	24.0	2.2	2.1	0.7
22	Perch	Luce	463753	853545	Inflow	213	30	0.0	100.0	0.0	330	6.9	14.0	2.2	5.2	0.7
23	Pretty	Luce	463603	853935	Inflow	229	30	12.9	100.0	0.0	60	6.4	13.0	2.3	2.5	0.6
24	Camp Eight	Luce	463557	854012	Seepage	230	30	0.0	100.0	0.0	95	6.6	14.0	2.9	2.5	0.6
25	Beaverhouse	Luce	463555	854045	Seepage	231	30	0.0	100.0	0.0	270	6.8	20.0	2.6	2.4	0.4
26	Muskallonge	Luce	464008	853800	Drainage	193	20	5.4	100.0	0.0	680	7.4	10.0	2.1	2.6	0.7
Noncalcareous moraine																
27	Garlinghouse	Chippewa	461745	843330	Seepage	222	45	66.3	0.0	100.0	−26	4.6	43.0	2.0	2.7	0.7
28	Avery	Chippewa	462435	844630	Seepage	270	45	0.0	0.0	100.0	−27	4.6	45.0	2.1	2.0	0.8
29	Bear	Chippewa	464207	851217	Seepage	231	20	55.3	0.0	100.0	−24	4.6	54.0	2.5	2.2	0.6
30	West Branch	Alger	463044	860605	Drainage	270	15	6.8	0.0	100.0	−16	4.9	70.0	2.1	2.3	0.7
31	McNearney	Chippewa	462538	845730	Seepage	264	35	0.0	0.0	100.0	−38	4.4	2.5	2.4	2.5	1.2
32	Stuart	Luce	463524	853035	Seepage	245	15	0.0	0.0	100.0	−17	4.8	6.4	2.3	1.8	0.7
33	Johnson	Chippewa	462530	850240	Seepage	252	30	0.0	0.0	100.0	−14	4.8	6.1	2.2	2.6	1.1
34	Kelly	Luce	462624	853840	Seepage	255	30	0.0	0.0	100.0	−5	5.2	7.6	1.9	2.1	0.8
35	Deadmans	Luce	462625	854143	Seepage	262	45	0.0	0.0	100.0	−5	5.4	10.0	1.9	2.1	0.6
36	Cusino	Schoolcraft	462716	861530	Seepage	267	15	0.0	0.0	100.0	−1	5.3	22.0	2.1	2.2	0.8
37	Stump	Chippewa	462155	845230	Seepage	272	20	0.0	0.0	100.0	14	5.7	20.0	2.2	1.9	0.7
38	Sand	Alger	463217	860520	Inflow	278	15	0.0	0.0	100.0	30	6.2	23.0	2.2	2.1	0.6
39	Murray	Luce	462815	854205	Inflow	272	60	0.0	0.0	100.0	31	5.8	20.0	1.9	2.1	0.5
40	East Soldier	Chippewa	462050	845125	Seepage	273	20	0.0	0.0	100.0	55	5.8	5.0	2.2	5.8	1.3
41	Keopfgan	Luce	463923	854633	Seepage	193	15	15.1	0.0	100.0	61	5.8	15.0	2.1	4.5	1.4
42	Bass	Luce	462749	854258	Drainage	273	60	0.0	0.0	100.0	110	6.6	14.0	2.2	2.1	0.5
43	Buckeye	Luce	462757	854419	Inflow	274	60	0.0	0.0	100.0	130	6.7	14.0	2.0	2.6	0.8
44	Peanut	Luce	462639	854327	Seepage	263	60	0.0	0.0	100.0	130	6.4	13.0	1.9	2.1	0.6
45	Nevins	Alger	463100	861435	Seepage	278	15	0.0	0.0	100.0	160	6.7	9.9	2.4	2.6	1.1
46	Sheephead	Chippewa	463827	851348	Drainage	217	30	80.1	0.0	100.0	240	6.5	150.0	2.2	4.1	0.8
47	Nugent	Alger	463138	861132	Seepage	274	15	0.0	0.0	100.0	250	6.6	7.5	2.1	1.9	0.7
48	Kinross	Chippewa	461645	843010	Seepage	222	50	7.4	0.0	100.0	600	7.1	42.0	2.1	33.2	0.9
49	Stanley	Schoolcraft	462919	860920	Drainage	260	15	0.0	0.0	100.0	820	7.8	30.0	2.0	1.7	0.7
50	Platt	Chippewa	462520	850030	Inflow	252	30	12.8	0.0	100.0	910	7.4	15.0	2.2	3.2	0.9
51	Ross	Schoolcraft	462847	861527	Inflow	265	15	0.0	0.0	100.0	1200	7.4	33.0	2.0	3.1	1.0
52	Belle	Luce	462902	854840	Spring	270	45	0.0	0.0	100.0	1300	7.4	3.1	2.0	2.3	1.0
53	Halfway	Luce	462825	853520	Seepage	253	30	0.0	0.0	100.0	1400	7.5	13.0	2.4	5.4	0.7

patterns. On the basis of these landform types, the 53 lakes were divided into three categories, shown in Table 3.

The first group is composed of 14 lakes and is located in the southern UP in thin calcareous till over carbonate bedrock. These lakes are generally characterized by high pH, with 13 of 14 having values ranging from 6.9 to 8.2 (mean = 7.39), and very high ANC ranging from 1100 to 8720 ueq/L (mean = 3754 ueq/L). The elevation of the 14 lakes (mean elevation = 220 m) reflects low relief and proximity to Lake Michigan (elevation = 179 m), and depth to bedrock is very shallow (mean = 5 m). About half the watersheds include some organic soil and four include lacustrine deposits, but the lakewater chemistry is dominated by inputs of mineralized groundwater. This is the same subset of lakes identified from chloride-based ECR values as being influenced by mineralized groundwater inputs. The exception is Tee Lake (lake number 13 on Fig. 1), which has very low ANC (37 ueq/L) and pH (5.8) compared with the other lakes in the group. Tee apparently receives little or no

Table 4. Sensitivity index based on acid neutralization capacity in relationship to geologic/geomorphic region.

ANC range (ueq/L)	Sensitivity category	Geologic/geomorphic region: Calcareous till		Lacustrine deposits		Noncal moraine	
<0	Acidic	0	0%	0	0%	10	37%
0–39	Extremely sensitive	1	7	1	8	3	12
40–199	Sensitive	0	0	2	17	6	22
200–499	Possibly sensitive	0	0	7	58	2	7
≥500	Not sensitive	13	93	2	17	6	22
		14	100%	12	100%	27	100%

groundwater input despite its similarities to nearby Stewart (14) and Mitten (12) Lakes, which are more typical of the group. Lake surface area and watershed size, mean lake depth, site elevation and depth to bedrock, and renewal times are very similar for the three lakes: hydrologic type is the only parameter that is different among the three systems. Stewart and Mitten are spring lakes, with permanent surficial outlets, whereas Tee has no surficial inlets or outlets, which implies that it is dominated by atmospheric rather than groundwater inputs. Tee appears to be a groundwater recharge lake whereas the other two are groundwater supported lakes.

The second group includes 12 lakes situated in glacial lacustrine deposits and is composed of circumneutral lakes (pH 6.7 to 7.4, mean = 6.9) of all hydrologic types. These lakes have the lowest site elevations of all the study lakes (mean = 208 m; Lake Superior elevation = 184 m). The ANC of these lakes ranges from moderately sensitive to not sensitive (<1000 ueq/L) and there appears to be buffering action in the watershed, perhaps due to the clay component of the lacustrine deposits. The three lakes (Andrus, Pretty, and Camp Eight) that have water chemistry different from the rest of the group are situated in sandy lacustrine deposits rather than clays and lack buffering or acid-neutralizing capacity in their watersheds.

The third category has 27 lakes located in noncalcareous moraine. Many of these lakes are in the sensitive or extremely sensitive ANC range (Table 4). The elevations of these lakes are the highest of all the study lakes (range 193 m to 278 m, mean = 255 m), and bedrock is buried beneath many meters of glacial drift (mean depth to bedrock = 32 m). The most striking feature of this set is that 37% of the lakes are acid (Table 4), that is, they have a negative ANC. This is the highest proportion of acidified lakes yet recorded in North America. In contrast, neither of the other two regions has any lakes in the negative ANC range.

Four lakes within this group are characterized by higher color (43 to 70 PCU). These have negative ANC (−16 to −27 ueq/L), pH's of 4.6 to 4.9, and large percentages of organic soils in the watersheds. Humic acids may contribute to the low pH in these lakes and metal complexation possibly affords some buffering capacity to these waters.

Another subset of 15 lakes in the group comprises generally clearwater, seepage lakes with ANC below 200 ueq/L and with no organic soils or lacustrine deposits in their watersheds. This group of lakes includes those already acidified and those most susceptible to continued acidic atmospheric loadings.

Eight lakes in the third group have high ANC and higher pH than most of the other lakes in this group. Of these, four (Piatt, Sheephead, Stanley, Ross) have surficial inlets with large watersheds (mean = 2530 ha) and high color values (mean = 56.9 PCU). Although these lakes are situated in morainal deposits that are not highly calcareous, there is apparently enough neutralizing capacity available (indicated by high SRI and ECR-chloride ratios) to neutralize acidic atmospheric inputs over an extended period of flow through the watershed. Belle Lake, a headwater lake, has a much higher ANC than the other lakes and is apparently supported by groundwater input high in calcium and magnesium, but low in the sulfate and chloride derived from evaporite deposits farther south. Although Halfway is defined as a seepage lake, with no surficial inlets or outlets, it also apparently has groundwater interaction, as indicated by its high ANC and pH and low SRI. Kinross, a lake with high color and an ANC of 600, is strongly influenced by anthropogenic activities. There is a large percentage of residential (37.5%) and agricultural use (8.8%) within the watershed. The high chloride value (110 ueq/L) is most likely the result of road salting in the area.

Correlation and Regression Analyses

Finally, the UP of Michigan provides an opportunity to examine relationships between watershed properties and associated lake chemistry for three contrasting sets of lakes. The first was the complete 53-lake set representing the entire north–south and east–west extent of the eastern Upper Peninsula with

Table 5. Selected correlation coefficients for watershed variables with acid-neutralization capacity, color, and sulfate for 53 Michigan lakes.

	All lakes—Correlation Coefficients		
	ANC[a]	Color[b]	Sulfate[b]
Area			
Lake surface area[b]	0.42**		
Total watershed area[b]	0.37**	0.32*	
Total watershed/lake area[b]		0.24	−0.26
Immediate watershed/lake area[b]	−0.27	−0.47**	
Hydrology			
Drainage order[b]		0.23	−0.33*
Total streamflow magn.—inlets[b]		0.36**	−0.29*
Total streamflow magn.—outlets[b]	0.30*	0.38**	
Maximum lake depth[b]	−0.30*	−0.41**	−0.50**
Mean lake depth[b]	−0.32*	−0.49**	−0.45**
Renewal time[b] (Mg^{2+})	−0.69**	−0.50**	−0.25
Relief			
Site elevation	−0.39**	−0.28*	−0.45**
Topographic high—immediate	−0.36**	−0.41**	−0.38**
Topographic high—total			−0.44**
Immed. watershed relief[b]		−0.36**	
Total watershed relief[b]	0.24		
Atmospheric influences			
Annual evapotranspiration	−0.31*		−0.57**
Annual acid input	0.54**		0.71**
Annual sulfate deposition	0.53**		0.71**
Bedrock			
Bedrock scale 1	0.32*		0.33*
Bedrock scale 3	−0.23		
Surficial deposits			
Depth to bedrock	−0.50**		−0.41**
Thin till over bedrock	0.54**		0.73**
Organic deposits		0.38**	
Lacustrine deposits			−0.25
Noncalcareous moraine	−0.50**		−0.32*
Vegetation			
Coniferous forest cover		0.27*	
Soils			
Loamy soils	0.58**		0.75**
Well-drained sandy soils	−0.58**	−0.40**	−0.60**
Nonacid organic soils[c]	0.49**	0.48**	0.29*
Acid-organic soils	−0.25	0.39**	
Clayey soils	0.28*		
Landcover–Land use			
Marsh		0.33*	
Transportation	0.23		
Cultural development[c]	0.23		
Extractive and cultivated[c]		0.28*	
Dwelling count/lake surface[c]		−0.41**	

* Significance <0.05 and ≥0.01. If there is no significance noted, it is 0.10 and ≥0.05. If there is no correlation coefficient, the significance is ≥0.10.

** Significance <0.01.

[a] Log_{10} transformation used with addition of a constant.

[b] Log_{10} transformation used.

[c] Square root transformation used.

ANC values ranging from −38 to over 8700 ueq/L. The second was a subset of 32 lakes, which, on the basis of ANC values of less than 500 ueq/L, are potentially sensitive to acidic atmospheric deposition (Glass and Loucks 1986). These lakes are located largely in the region of Cambrian sandstone and thick noncalcareous morainal deposits in the northern half of the peninsula.

Tables 5 and 6 summarize selected correlation coefficients from the large correlation matrices for the 53-lake set (Table 5) and lower ANC subsets (Table 6). The variables in these tables were selected on the basis of strength and significance of individual coefficients and on the basis of the likelihood of affecting ANC, color, and sulfate.

For the entire lake set (Table 5) acid-neutralization capacity is most strongly correlated with lakewater renewal time, atmospheric inputs, depth to bedrock, and surficial deposits, including landform and soil type, which are closely related. The excess Ca^{+2} and Mg^{+2} available from the easily weathered limestones and dolomites in the southern UP, where depth to bedrock is 1 m or less, produce lakes such as those on Drummond Island with very high cation concentrations and ANC values of over 5000 ueq/L. ANC is also related to lake and watershed size as shown by the strong positive correlations with lake surface area and total watershed area. For example, Muskallonge and Piatt are large lakes with large watershed drainage areas and ANCs of 680 ueq/L and 910 ueq/L, respectively.

Color is related to soil type and correlates strongly with hydrology and land-use factors. It correlates positively with organic soils, rich in the natural humic acids that contribute to metal complexation, and negatively with well-drained, sandy soils having little organic acid and short retention times. Garlinghouse, with 66%

Table 6. Selected correlation coefficients for watershed variables with acid-neutralization capacity, color, and sulfate for 32 Michigan lakes (ANC <500 ueq/L) and 23 Michigan lakes (ANC <200 ueq/L).

	Low-Alkalinity lakes—Correlation Coefficients					
	ANC[a]		Color[b]		Sulfate[b]	
	32 lakes	23 lakes	32 lakes	23 lakes	32 lakes	23 lakes
Area						
Lake surface area[b]	0.32					
Total watershed area[b]	0.34		0.42*			
Immediate watershed/lake ratio[b]			−0.32			
Hydrology						
Total streamflow magn.—inlets[b]	0.47**		0.37*		−0.31	−0.48*
Total streamflow magn.—outlets	0.36*		0.58**			
Mean lake depth[b]			−0.40*	−0.40		
Renewal time[b] (Mg^{2+})	−0.44*		−0.54**	−0.42*		
Relief						
Site elevation	−0.41*		−0.36*			
Topographic high—immediate			−0.45**			
Topographic high—total			−0.32			
Atmospheric influences						
Annual evapotranspiration		0.51*			−0.37*	
Annual acid deposition		−0.46*			0.32	
Annual sulfate deposition		−0.48*			0.35*	
Bedrock						
Bedrock scale 1	−0.37*		−0.30			
Bedrock scale 9	0.33					
Surficial deposits						
Organic deposits			0.30			0.36
Lacustrine deposits	0.54**					
Noncalcareous moraine	−0.61**	−0.42*				
Vegetation						
Coniferous forest cover	0.43*		0.31			
Soils						
Well-drained sandy soils			−0.52**	−0.41		
Nonacid organic soils[c]	0.46**		0.33			
Acid–organic soils		−0.39	0.57**	0.49*		
Landcover–Land use						
Cultural development[c]					0.30	0.37
Dwelling count/lake surface[c]			−0.59**	−0.69**	0.30	

* Significance <0.05 and ≥0.01. If there is no significance noted, it is <0.10 and ≥0.05. If there is no correlation coefficient, the significance is ≥0.10.

** Significance <0.01.

[a] Log_{10} transformation used with addition of a constant.

[b] Log_{10} transformation used.

[c] Square root transformation used.

acid organic soil in the watershed, has a color value of 43 PCU, whereas Kelly, with 95% well-drained, sandy soils has a color of only 7.6 PCU. Small lakes with little surficial flow, such as Stump and Avery, tend to be highly colored. The strong negative relationships between color and dwelling/lake area and road length (-0.46, $p < 0.01$) may be related to the undesirability of locating a cabin or dwelling on small lakes with highly colored waters.

Sulfate correlates strongly with hydrology, surface deposits and soils, and atmospheric inputs. In the southern Upper Peninsula elevations are lower, lakes and surficial deposits are shallower, and soils are loamy and related to calcareous moraines. In this area highly mineralized groundwater seepage is indicated by extremely high sulfate (26 mg/L) and chloride (5 mg/L) concentrations in the lakes. Wet sulfate deposition increases to the east, but the high in-lake sulfate values are mainly the result of groundwater influx that overwhelms the influence of wet sulfate deposition: the strong correlation with wet sulfate deposition is a coincidence in the 53-lake set.

Because ANC and sulfate concentrations are so strongly tied to regional geology and mineralized groundwater input, the influence of calcareous bedrock and surficial deposits was limited by selecting the low ANC subsets of lakes located in the northern part of the peninsula. Table 6 summarizes the selected correlation coefficients from the matrix for these subsets. Here, the interrelationships between variables are more limited, and a truer signal is indicated by significant correlations.

For the 32-lake subset, ANC is still strongly correlated with landform type, positively with lacustrine deposits where clays are likely to provide buffering capacity (e.g., in lakes Pendills and Monocle), and negatively with percentage of noncalcareous moraine where there is a distinct lack of neutralizing or buffering capacity (e.g., in lakes Murray and Deadmans). ANC also is strongly related to lake type as defined by streamflow magnitude. Seepage lakes, such as Johnson and Andrus, with no surficial inflow, are often precipitation-dominated and are more sensitive to atmospheric inputs. Color is again related to organic soils and lake hydrology. Sulfate correlates with hydrology, atmospheric inputs, and land use. When the 23 lakes within the ANC categories of sensitive, extremely sensitive, and acid (Table 4) are examined together (Table 6) and as individual subsets, atmospheric influence factors (acid and sulfate deposition) emerge as significant negative correlates with ANC, indicating strong dominance of lake chemistry.

Following development and interpretation of the correlation matrices, three sets of multiple regression runs were performed on dependent variables ANC, sulfate, and color for each of the three lake sets. Multiple regressions on the 23-lake subset proved inconclusive (due to the small sample size). For the 53- and 32-lake sets, however, this technique provided additional insight into watershed interactions and processes.

The variability in each of the dependent variables (ANC, color, sulfate) for the 53- and 32-lake sets is best accounted for by the independent variable subsets listed in Table 7. For each dependent variable, this table lists the independent variable subset that conforms to the following criteria: (1) a higher adjusted r^2 (correlation coefficient) than any other subset; (2) absolute values of all T-statistics for each variable in the subset greater than 2.0; (3) a Mallows Cp as low as possible, but greater than the number of independent variables used in the regression. These "best subsets" point to watershed component variability factors (and therefore to differences in terrestrial processes across the region) that correlate strongly with the sensitivity of lakewaters to acidic input. The nature of the relationship between these best subset components and the dependent variables is further illuminated by considering the magnitude, direction, and significance of each in direct correlation with the dependent variable (as in Tables 5 and 6).

Table 7. Best regression subsets for Michigan watersheds.

A. All lakes (n = 53)	ANC	Color	Sulfate
Total watershed area	X		
Total streamflow magnitude—inlets		X	X
Mean lake depth		X	
Renewal time	X		
Loamy soils	X		X
Nonacid organic soils	X	X	X
Acid organic soils	X	X	
Thin till over bedrock			X
Cultural development	X		
Adjusted r^2	0.76	0.60	0.67
B. ANC <500 ueq/L (n = 32)	**ANC**	**Color**	**Sulfate**
Total watershed renewal time		X	
Mean lake depth		X	
Total streamflow magnitude—inlets	X		
Annual evapotranspiration			X
Noncalcareous moraine	X		
Acid–organic soils		X	
Dwelling/lake ratio		X	
Adjusted r^2	0.53	0.67	0.14

As a primary sensitivity indicator for the 53-lake set, ANC can be "explained" in large part (Table 7A) by its positive correlations with total watershed area, loamy soils, nonacid organic soils and cultural development, and its negative correlations with renewal time and the presence of acid-organic soils. The most susceptible lakes, those with low alkalinity, were found in areas with small catchment basins, acid soils, little direct cultural influence, and longer lake renewal times.

Color correlated positively with the presence of organic soils (acid and nonacid) in the watershed and negatively with the mean depth of the lake and the ratio of immediate watershed to lake surface area. As an indicator of sensitivity, it may be seen that low-color lakes were primarily associated with the absence of organic soils, shallow lake beds, and low basin/lake size ratios that indicate that the lake receives a high ratio of atmospheric inputs unmitigated by terrestrial sources.

Sulfate was found to be explained by its positive correlations with loamy and nonacid soils as well as the presence of thin till over bedrock. It must be noted here that many of the thin-till lakes were located on Drummond Island at the farthest eastern end of the

study region. With this in mind, the thin-till correlation may be seen as a surrogate for atmospheric sulfate deposition (which is highest in this portion of the Upper Peninsula).

When the 32 lakes with ANC values less than 500 ueq/L are examined separately, the effects of parameters dominated by calcareous surficial deposits and bedrock are eliminated (Table 7B). The amount of variability that can be explained decreases for ANC and sulfate in each category, yet for each dependent variable, new factors emerge that point to important processes within this potentially sensitive group.

The variability in ANC within the low ANC group can now be seen to be accounted for by its positive correlation with streamflow magnitude and a strong negative correlation with the presence of noncalcareous moraine. Sensitive lakes (with ANC <500 ueq/L), therefore, tend to be those with low-volume surface-water inputs.

Color continues to reflect the presence of organic soils with positive correlations with sandy and acid-organic soils, while mean depth and renewal time correlate negatively, indicating loss from decomposition (Schnoor and Stumm 1984). There is very little difference between the watershed component subsets explaining color's variability across all 53 lakes or within the 32-lake set.

No best subset could be derived for sulfate for the 32-lake set as no grouping of variables could be made that accounted for more of the variability in lake sulfate than the single-factor correlation with evapotranspiration could (see Table 6).

Conclusions

The questions of interest in this article have been (1) the overall pattern and range of lakewater chemistry and watershed characteristics for a region of sedimentary bedrock, and (2) how the 53 lakes in the region differ in sensitivity to acidic deposition from those on the Canadian Shield evaluated in previous studies. The results show that in this region, despite glacial reworking, the acid-neutralizing potential from calcareous substrates extends very little northward into updrift areas with low acid-neutralizing capacity. Although groundwater in much of the calcareous zone has been enriched with sulfate and chloride from nearby gypsum and anhydrite deposits, these influences do not seem to affect surface waters in aquatic systems north of the calcareous substrates.

When the study area is divided into three geomorphic regions—one along Lake Michigan underlain by calcareous bedrock, one to the north along Lake Superior associated with glacial lacustrine deposits, and the third in the higher elevation, noncalcareous morainal region between the two lakes—marked differences between the regions are found. The first region is characterized by shallow soils and drainage systems apparently influenced by mineralized groundwater inputs. The lakes are high in pH and alkalinity despite high sulfate concentrations in the surface waters. The second region is characterized by lakes with pH in the range of 6.5 to 7.0 and ANC below 500 ueq/L. The third region is distinguished by a high frequency of seepage lakes scattered in the moraine and outwash. Thirty-seven % of the lakes studied in this region are acid (i.e., have negative ANC), the highest for any contiguously distributed population of lakes yet studied in North America. The significant negative correlation of atmospheric inputs with ANC in these lakes indicates the dominance of atmospheric factors over watershed factors in the control of lakewater quality.

Regression analyses show that the variability in three lakewater sensitivity indicators (ANC, color, and sulfate) can be largely accounted for by considering the watershed components and atmospheric inputs. ANC was found to be related to hydrology and soils or surficial deposit factors across the entire 53-lake set and within the 32-lake group. Color was correlated with organic soils and hydrologic factors in each lake set. Lake sulfate was correlated with the atmospheric sulfate deposition and other atmospheric input indicators (see Table 6). The hypothesis that atmospheric inputs are important in determining lake chemistry is confirmed for lakes with watersheds on silicious sedimentary rocks.

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